RECENT ADVANCES IN ANALYTICAL CHEMISTRY

BY

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INTRODUCTION

Before starting a discussion of recent advances in analytical chemistry, a side excursion will be taken into the field of the nature of analytical research and the recent trends in its development.

The analytical chemist, in past years, has been called upon to determine the type and amount of a particular substance under test. Recently, in addition to this, he has been asked to determine questions of structure. This last topic is but a natural concomitant of the answer to the basic question asked of the analytical chemist: "What is it?" To answer this question by telling what substances are present and in what amount is not the full nor desired description. A gross example will perhaps bring this point more clearly into focus. If the Empire State building in New York City were placed for analysis (i.e."What is it?") before an analytical board it is obvious that the answer of the numbers of girders and bricks together with their composition does not describe the object fully. The analyst must also present the structure as an integral part of his report in order to delineate the substance most exactly.

This question of structure has long been recognized in organic chemistry as one of prime importance but has only recently come to the fore in inorganic analyses. This is in spite of the fact that , in their search for a specific reagent, the chemists have so far found only those which strongly suggest that they are

specific for a certain structure (or conversely, that the structure of the reagent is specific for the element under test. The trend now fortunately is to do basic research in the field of molecular structure and to plan an intelligent search for specific reagents. This fruitful field of analytical research has only had its surface cursorily scratched by chance and not developed by science.

The paths of research are in general twofold:

(1) Development of new, more accurate techniques.

(2) Development of new principles.

Both of these paths should be fully explored and to develop one at the expense of the other is to be both short sighted and impractical.

In this paper, two recent advances, which embody both of the above principles, will be surveyed. These two fields are:

(1) Chromatography

(2) High frequency titrimetry

CHROMATOGRAPHY

In the opening remarks it was noted that a trend toward structural specificity is being followed in analytical chemistry. There is no better example of this than in the field of chromatography. First exploited by Tswett in 1906 it can now, in some cases, meet the requirements for quantitative separation of specific structures.

Unfortunately, the lack of basic research noted above, has hampered the development of this technique and has lead to "cook book" chemistry in this field. As yet, for example, there is no completely satisfactory theory which can predict the adsorptive power of different materials under varying conditions. As a consequence, the results to date have fallen short of the potentialities of this analytical process.

General

Chromatography may be defined as a method of separation based on differential adsorption, i.e., the differential partition of solutes between a moving and a stationary phase. It has been compared to fractional distillation due to the fact that the adsorption is a repeated process (18). The flow of solvent which contains the unknown forces it through the adsorbent and the competing phases attract the adsorbate by various means. Due to the differential adsorption, the unknown forms a band or separate entity and is further separated (developed) by the flow of pure solvent.

The unknown can be tested for by elution analyses or frontal analyses. In the latter case, the unknown is forced through the adsorbent and out of the adsorbent phase. Then the effluent is analyzed at various intervals. In elution analyses, the unknown is kept in the adsorbent and then this portion analyzed. In this type of adsorption analyses the competing phases are not limited to the usual moving liquid-stationary solid adsorbent types but can cover any combination of phases.

There are several types of chromatographic analyses, all based on differential migration:

1. Adsorption
2. Paper
3. Ion exchange

None of the mechanisms associated with the above types is clearly understood, although efforts have been made to approach the problem from a theoretical viewpoint (4) (14). In these treatments, attempts to set up workable relations between the variables have been made. These are approximations, however, since the very physical nature of the process is not known. Thus a theory on which to base predictions is not presently available. By an inspection of the variables presently thought to be involved in the chromatographic process it can quickly be seen that it will take an army of chemists several lifetimes to explore all the possible permutations of these variables. Therefore, the need for basic research on which to base statistically designed experi-

ments remains a vital need in this field.

The variables affecting the efficiency of the chromatographic process are, in part, as follows (11):

1. Physical state of adsorbent and adsorbate
2. Structure of adsorbing surface
3. Physical condition of adsorbent
4. Degree of dispersion of adsorbed solutes
5. Relative concentration of solutes
6. Nature of solvent
7. Chemical nature of solutes and adsorbents
8. Temperature

In addition, since this is a problem in differential migration, the ratio of the rate of movement of the adsorbed compound to the rate of movement of the developing solvent is the most important index of the process.

Once the adsorption has been accomplished, the limits of the adsorbed phase must be determined. The methods presently used are (1):

1. Direct visual inspection
2. Fluorescence in ultraviolet light
3. Color change in stationary indicator
4. Radioactive indicators
5. Optical techniques in the effluent
   a) Refractive index
   b) Interferometric methods
   c) Thermal conductivity

It should be noted here that any new method of identifying zones will present an important but not a significant advance in this field.

At this point, the field of electro chromatography will be dealt with briefly. This method differs from the flow of solvent method only in the driving force which is an electric field in this case (19). The method can be used only if the unknown is in the ionic form. The competition of the various phases for the unknown is still present and gives the same results as other methods.

Recent comprehensive reviews in the field of inorganic adsorptive chromatography attest to its growing importance as a tool of the chemist (17). Although analyses have been performed on some compounds with satisfactory accuracy, the advent of a workable theory should bring many more substances into the scope of this type of analysis.

The mechanism of adsorption between different phases such as solid-gas and liquid-liquid (15) has been studied to some extent and valuable contributions made. The solid-gas adsorption is of much interest in the "alchemy" of catalysis. In this relation, the variation of pressure will introduce an important new variable into chromatography. It appears that investigations involving the gaseous phase could be more profitably pursued in investigating the mechanism since we have the proven theories of the gaseous state as a basis for investigation.

Paper Chromatography

Paper chromatography is essentially a technique, rather than a new principle. It has become so popular in the last five years that it has appropriated a field of its own for research endeavor. The principle of differential migration is still present, but in this case the adsorbent is held by paper and the adsorbate is allowed to proceed under various driving forces along the paper and thus permit the competition between phases for the adsorbate to effect the separation.

The advantages of this system are simplicity, inexpensiveness, flexibility and adaptability. Qualitative analyis can be carried out by observance of the developed "spot" on the paper and quantitative analysis effected by the use of a densitometer.

This type of chromatography is often called partition chromatography because the two liquid phases (one immobile in the cellulose of the paper; the other the moving solvent) compete for the solute which distributes itself between each phase in the ratio of the solubility in each phase. The usual principle of distribution holds in this case i.e.

$$\frac{\text{conc. phase I}}{\text{conc. phase II}} = \text{constant}$$

If two spots appear close together, they can often be resolved by:

1) Electric means

2) Two dimensional analysis

This latter method employs the use of a different solvent flowing at right angles to the original solvent.

There have been no general mathematical treatments of the above problem which allow predictions to be made of the types of substances and the amounts partitioned. The field of solubility is better documented and more is definitely known about its mechanism than is known about the mechanism of adsorption. For this reason, it is plausible to state that this field will be the first to produce a theory which can predict which solvent will separate a given constituent.

One of the variables in this method of analysis is the type of paper being used. However, if standard filter paper is used this variable has little effect.

It has been found (8) that the radius of the zone formed on the paper is a function of the sum of the logarithm of the concentration and a constant depending on the paper, i.e.

$$r = f(\log C + A)$$

Therefore, the size of the zones gives an indication of the amount of material present. The positions of the different zones are also important since their (the zones') motion down the paper seems to be a function of the unknown under consideration and the solvent providing the driving force. In this way, various constituents can be identified without other treatment.

At best, however, the selection of solvents is empirical but the flexibility of this method in dealing with minute quantities

is so marked that the field is now under intensive investigation. A review by Clegg (5) gives a lucid account of the subject.

Ion Exchange

The third division of chromatography which will be considered is ion exchange. The search for a specific reagent is being diligently carried on in the form of a search for a specific resin for each element. Since, as in the previous fields, the mechanism is not completely known, the search has not come to its goal.

This exchange is thought to be wholly surface reaction. It can be thought of as a dynamic exchange caused by the statistical bombardment of the exchange resin by the flowing substance. In this way an equilibrium is set up at the surface.

Another possibility for this mechanism is that it is caused by the surface ions of the resins having a residual valence and being easily solvated. Thus the lattice bond is broken more easily and the lattice ion can be exchanged for an ion in solution.

There are two types of exchangers depending for their exchange properties on the functional groups present:

1) Anion exchangers (NH_2, NHR, NR_2)

2) Cation exchangers (SO_3H, COOH, OH)

There are several well known inorganic exchange reactions that have been used extensively in water softening. Examples of these are:

$$NaZ + Ca^{++} \qquad Na^{+} + CaZ$$

$$NaP + Ca^{++} \qquad Na^{+} + CaP$$

One of the main requirements for an exchange resin is its "absolute" insolubility in the medium which carries the unknown. This insolubility must be much less than that of several salts now thought insoluble. One solubility product constant should be so low as to allow continuous operation of the ion bed without exhausting the exchanger. The bed can be recharged but only if it has not been dissolved by the medium carrying the unknown.

There have been several attempts to solve the theory of exchange by the Gibbs-Duhem equation, but the approximations made have been so drastic as to render any generalizations impossible. Even with the approximations, the theory arrived at is almost hopelessly complicated and incapable of application. Therefore in this field also equations are empirical and predictions unreliable.

According to Kunin (13), the extent of exchange depends on:

1) Forces binding ions and lattice
2) Relative valencies
3) Total concentration
4) Sizes of ions
5) Accessibility of lattice ions
6) Solubility effects

The following rules are also qualitatively obeyed:

1. With low concentration of aqueous solution and at room temperature the exchange potential varies as the valence of the exchanging ion.

2. At low concentration and room temperature at constant valence the exchange potential varies as the atomic number.

3. At high concentration the difference in exchange potential decreases and in some cases the ion of lower valence has greater exchange potential.

4. At high temperature, non aqueous media, and high concentration the exchange potential of ions with the same valence does not increase with increasing atomic number.

5. Activity coefficient varies as the exchange potential.

From the above discussion it appears that an equation could be arrived at from the theory but the difficulty lies in the fact that theory is vague and uncertain. For example, to say that exchange depends on forces binding ions is certainly true but almost quantitatively useless unless these forces are investigated and specified. This is likewise true of the catch-all "solubility effects". The similarity between exchange rate and ionic strength is pointed out in the first qualitative rule and seems to be one road out of the maze, since the activity coefficient does vary with the exchange potential. The work on

activity coefficients can thus be correlated with ion exchange to try to produce a workable theory.

In the above brief discussion of chromatography it should be noted that, although the potentialities are great, so are the obstacles. There is no present workable theory which can predict accurately the various chromatographic parameters. Here, as was pointed out in the opening paragraph, is a field for structural inorganic analysis so that the shapes and means of bonding might be investigated to provide a firm basis for theory. There must be systematic and intelligently planned research in order to get the task accomplished in a minimum period of time.

Summary of Electrical Terms Used in High Frequency Titrimetry

Term	Symbol	Magnitude
Admittance	Y	$\sqrt{G^2+B^2} = \frac{1}{Z}$
Conductance	$G_{Hi\ Freq.}$	$\frac{1}{R_{hi\ Freq.}}\ \frac{R_{DC}}{R_{DC}^2+X^2}$
Reactance	X	$2\pi fL = \frac{1}{2\pi fC}$
Susceptance	$B_{Hi\ Freq.}$	$\frac{X}{R_{DC}^2+X^2}$
Impedance	Z	$\sqrt{R_{DC}^2+X^2}$

These relationships can be obtained from general expression for impedance:

1) $Z = R-JX$ (For capacitive reactance)

2) $Y = \frac{1}{Z} = \frac{1}{R-JX}$

rationalizing

3) $Y = \frac{R+JX}{R^2+X^2}$ and separating into real and imaginary parts

4) $Y = \frac{R}{R_2+X^2} + \frac{J\,X}{R^2+X^2} = G + JB$

HIGH FREQUENCY TITRIMETRY

In volumetric analysis, the determination of end points by electrometric means instead of indicators has become an important practice in many laboratories. It has come to the fore as an important method because it is accurate, rapid, and adapts itself to automatic and recording procedures.

The properties of any electric circuit of which a titration cell is a specific type can be grouped under the following headings:

1) Direct current properties
2) Alternating current properties

We may think of the direct current properties as intrinsic properties, independent of the impressed signal. On the other hand, the alternating current properties are functions of the frequency of the impressed signal.

The investigation of direct current properties as functions of concentration of electrolyte led to the familiar conductometric, polarographic or amperometric, and potentiometric methods of titration employing the D.C. circuit parameters of voltage, current and resistance as criteria of the progress of the titration.

The logical extension of electrometric work is the investigation of alternating current properties as a function of concentration. This is being attempted in the field of high frequency titrimetry.

Many of the titrations in direct current work do not give sharp enough end points for accurate analytical work so an

electrometric titration, based upon alternating current properties (3) has been used.

It is appropriate here to go into the theory of the solution as a circuit element prior to treating the element by circuit analysis.

To start this discussion we will first investigate that portion of the electromagnetic spectrum in which we are interested and see what periodic phenomena exist in this range. Since we will be dealing with ions in solution, we want a periodic characteristic of these ions that will respond over a given band of frequencies. The concept of relaxation time of the ionic atmosphere proposed by Debye and Falkenhagen (7) supplies the periodic characteristic. Now we must investigate the range of frequencies over which this characteristic is dominant. Before doing this, however, a numerical example will be given to point out the orders of magnitude involved and the relation of this relaxation time to other dipole orientation periods.

For example, at 30,000 megacycles, the value of the energy associated with this vibration is 1.98×10^{-16} ergs obtained from: Energy = $h\nu$ where h is Planck's constant and ν the frequency. To put this value into terms more familiar to the chemist we perform the following operation:

$$\frac{\text{ergs}}{\text{molecule}} \times \frac{\text{molecules}}{\text{mole}} \times \frac{\text{calories}}{\text{erg}} = \frac{1.98\times10^{-16}\times6.02\times10^{23}}{4.18\times10^{7}} = 2.86 \ \frac{\text{calories}}{\text{mole.}}$$

This is a very small value of energy and is much less than the

ordinary separation between electronic and vibrational levels. However, on investigating the rotational levels of linear molecules we find separations of the order of 0.55×10^{-16} ergs, which shows that the above frequency is in the range of rotational absorption energies.

Now, at longer wavelengths, we should expect to leave the realm of molecular internal energy levels and reach that due to the gross movement of the molecule itself. The molecular, or dipole orientation, has been investigated and found to have a value of about 1600 megacycles for a measured period of about 10^{-10} seconds. This period is called the molecular relaxation time and is the time to return to normal position after the field has been removed. This corresponds to the resonant or in phase feeding in of energy common to all oscillating systems. From the representative values given it can be seen that the molecular orientation corresponds to a less energetic part of the electramagnetic spectrum than the rotational absorption levels.

If we proceed to still lower frequencies we find that the relaxation time of the ionic atmosphere begins to appear. This atmosphere changes with the impressed field but its natural period is independent of the driving frequency. It is important here to differentiate between the natural or resonant frequency and the frequency of the driving force. When these two are equal it means that maximum energy is being transferred to the system.

For an electrical circuit in which we are postulating (1) no inductance (2) the electric field does not affect the structure of the ion, the following discussion will apply.

Power dissipated in a circuit follows the following expression:

1) $P = EI\cos\Theta$ where Θ is the angle between the current and applied voltage.

From Ohm's law for an A.C. circuit:

2) $I = \frac{E}{Z}$ where Z is the complex impedance given by the expression R + JX

Combining 1) and 2) we have:

3) $P = \frac{E^2}{Z}\cos\Theta$

But Z is related to the resistance by: $Z = \frac{R}{\cos\Theta}$ (4)

so that 3) becomes:

$$P = \frac{E^2}{R}\cos^2\Theta$$

Now defining G = conductance = $\frac{1}{R}$ we have for the final form:

$$P = GE^2\cos^2\Theta$$

Examining this expression for maximum power we see that for a constant impressed voltage, the power varies as $G\cos^2\Theta$. For maximum conditions, this product must be a maximum and this

will occur when both G and cos Θ are maximum simultaneously. The maximum value of the cos Θ is unity when the driving force and follower are in phase. Assigning a value of G_{max} to maximum conductance we see that maximum power occurs at unity power factor and a value of G_{max}.

In addition, the in-phase condition implied by unity power factor, imposes the restriction that, at this time, $W\Theta$ = unity where $W = 2\pi\nu$ and Θ = relaxation time of the ionic atmosphere. This states that the impressed and natural vibrations are in phase at the unity power factor - maximum power point.

To eliminate the power dissipated restriction, we can say that:

Power transferred = power dissipated + power stored

Placing the appropriate expressions in the right hand side of the above equation we have:

$$\text{Power} = E^2G + \tfrac{1}{2}CE^2 \quad \text{where } C = \text{capacitance}$$

From this equation it can be seen that for a given impressed voltage the power transferred is a maximum:

a) when G is a maximum

b) when $\frac{C}{2}$ is a maximum

These are, therefore, separate but dependent conditions which must be fulfilled simultaneously for maximum power transfer.

In addition the following conditions likewise apply:

a) Power factor equals unity

b) $W\Theta$ equals unity.

If the above conditions are not met then maximum power will not be transferred. This is stating physically that there is a frequency beyond which the follower cannot follow the driver and leads to the general picture shown in Figure 1.

The general expressions and concepts used above are applicable to any oscillating system. An electrical analogue is not the only type which can be derived, but it is used because the methods of electrical analysis and measurement offer great facility in the solution of physical problems.

Debye-Falkenhagen Equation and Experiments

Debye and Falkenhagen (7) derived a relationship for ionic relaxation time as follows:

$$\Theta = \frac{8.85 \times 10^{-11} \times D_o}{\Lambda_\infty \times \gamma}$$

D_o = dielectric constant of solvent

Λ_∞ = equivalent conductance at infinite dilution

γ = concentration in $\frac{\text{g equiv.}}{\text{liter}}$

This was verified experimentally by Forman and Crisp (9). However, they found that at certain values of γ giving corresponding relaxation times, that the dielectric constant of the solvent does not have its characteristic value but suffers dispersion. This implies a changing capacitance since the capacitance and the dielectric constant are directly proportional. Both the Debye-Falkenhagen and Forman-Crisp calculations are based on

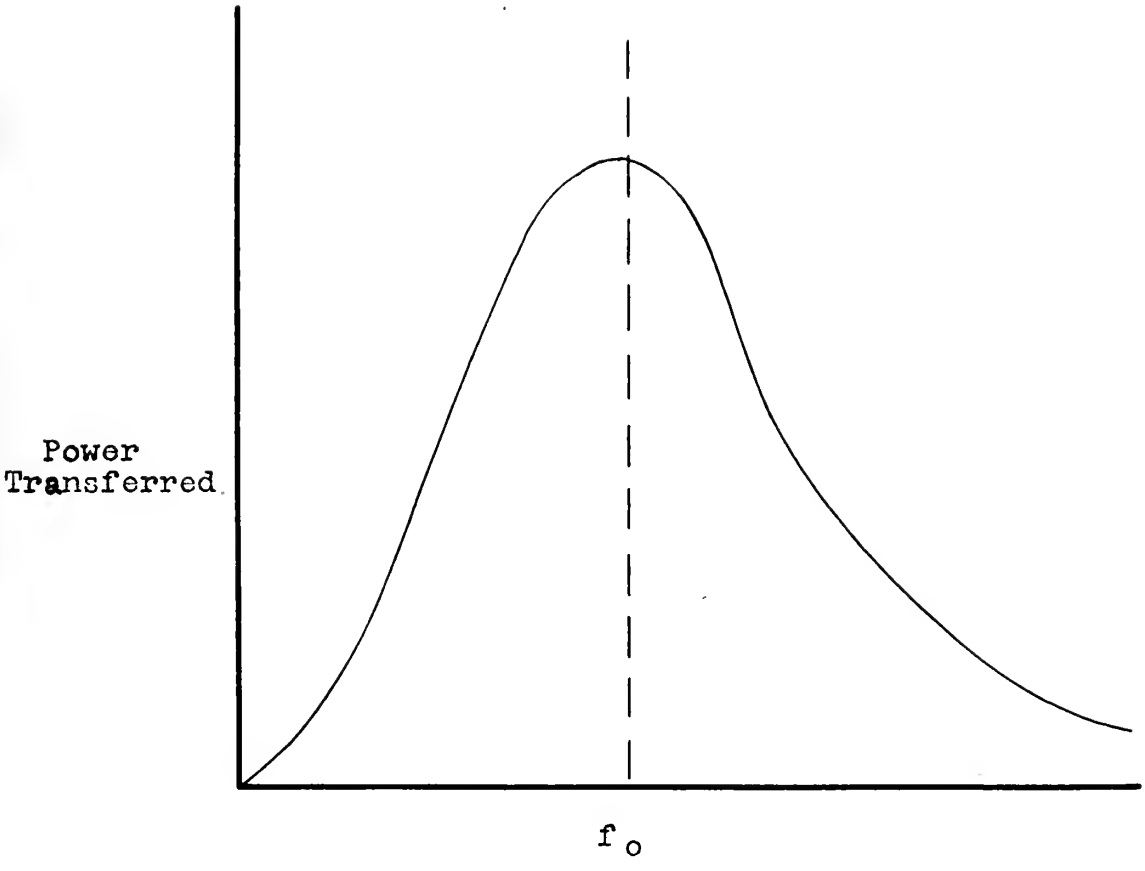


Figure 1

extremely dilute solutions as can be seen by the inclusion of Λ_∞ in the derived expression. In this case the dielectric contribution from the electrolyte is small in comparison to that of the solvent and therefore D_o can be used although it appears that what is actually meant is $D_{solution}$. The dispersion is detected because the contribution of the electrolyte is not uniform but changes rapidly in the neighborhood of resonance. This rapid change in the vicinity of resonance is not startling in the light of the behavior of other circuit parameters in this range (Q curves). The behavior discovered by Forman and Crisp is reproduced qualitatively in Fig. 2.

This shows that the frequency is a function of concentration and thus the capacitance which is related to the concentration through the dielectric constant.

In addition to this, Forman and Crisp found that the energy absorbed varied with the concentration and that the concentration corresponding to maximum energy was the same as that corresponding to the resonant frequency. Therefore, we can see that simultaneous conditions postulated on general physical principles are met experimentally.

The following relationship predicted by Debye and Falkenhagen was proven empirically by Forman and Crisp:

$\lambda_{max}\gamma = K_e$ where λ_{max} is the wavelength for maximum absorption and K_e is a characteristic constant depending on

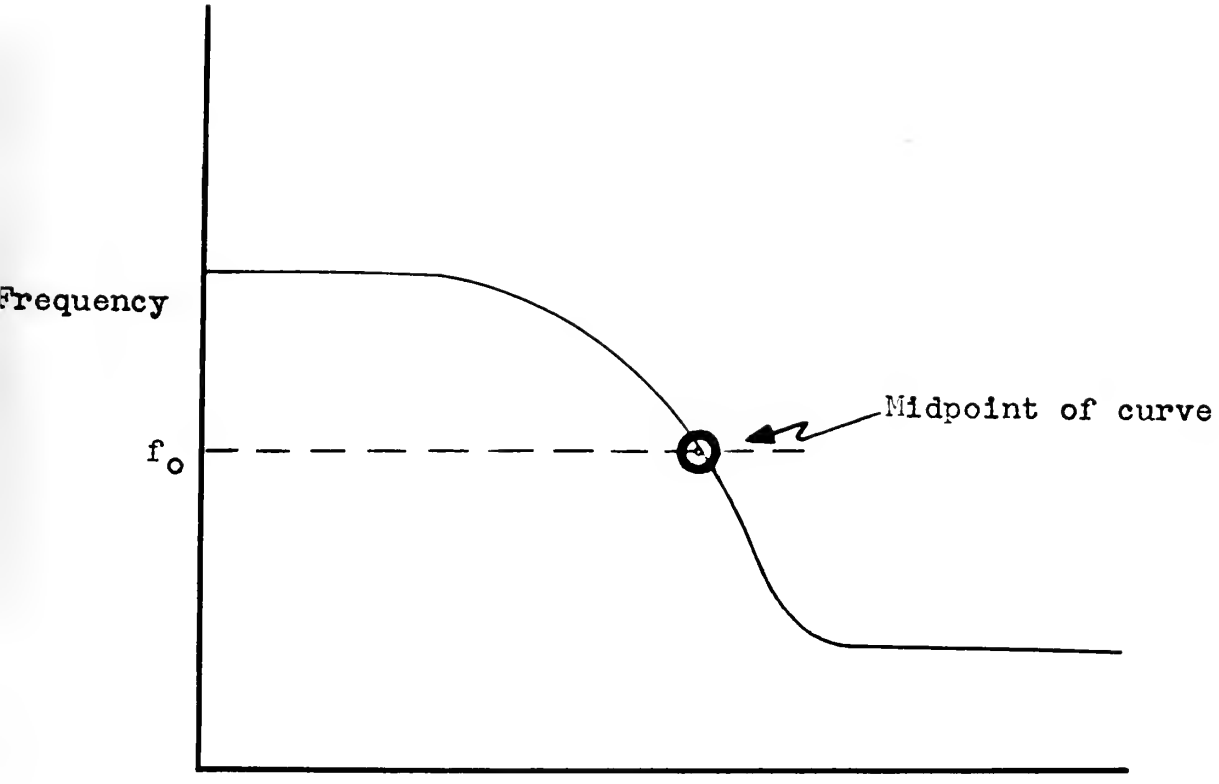


Figure 2

the electrolyte. This can be shown from the Debye equation as follows:

1) λ_{max} implies $\textcircled{H}$ resonant by definition

2) $\textcircled{H}_{max} = \frac{1}{W_{max}}$

3) $\frac{1}{2\pi\nu_{max}} = \frac{8.85 \times 10^{-11} \times D_o}{\Lambda_\infty \times \gamma}$

4) $\frac{1}{\nu} = \frac{\lambda}{C}$ where C = speed of light

5) $\lambda_{max} = \frac{2\pi \times C \times 8.85 \times 10^{-11} \times D_o}{\Lambda_\infty \times \gamma}$

6) $\lambda_{max}\gamma =$ K_e which for a given solvent, is characteristic of the electrolyte since it depends on Λ_∞

The similarity between the above equation and that for black body radiation is striking. In black body radiation the Wien displacement law states:

$\lambda_{max} T$ = Constant where T is the absolute temperature and λ_{max} is as defined above. Since the relation was derived from the theory of oscillators we see that the "relaxation oscillator" postulated for the solution fits into previous concepts. In fact, as will be shown later, the curves of high frequency conductance which we have shown to be directly proportional to power, versus concentration give the same appearance as those for

black body radiation. This is not coincidence since it points out the fact that the phenomenan considered depends on the range of the spectrum being investigated. The same general laws hold throughout the range from alternating current to cosmic rays.

We will now formulate an electrical circuit which will have the following characteristics:

1) A period of oscillation which will vary with the resistance and capacitance.

2) Power loss to go through a maximum at some resonant frequency.

3) This resonant frequency to correspond to that frequency at which:

a) G is a maximum

b) $\frac{1}{2}C$ is a maximum

4) Unity power factor to occur at resonant frequency.

By inspection of the Debye-Falkenhagen equation, we see that the term $\gamma\Lambda_\infty$ appears. Now by definition:

$\gamma \times \Lambda = 1000 \times K$ where K is the specific conductance

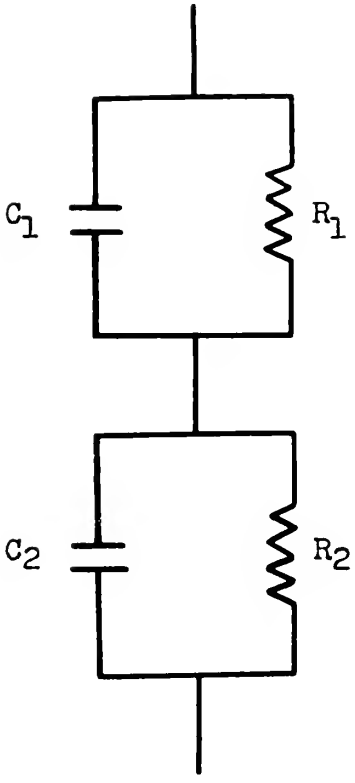
Therefore, our equation in which Λ_∞ appears is good only for dilute solutions and is, therefore, restricted. This dilute solution restriction was also mentioned above in the discussion of the dielectric constant term of the equation. Since we have

a dielectric constant and a conductance appearing this immediately suggests a resistance and capacitance for our circuit elements. This suggestion is added further weight by the fact that a resistance-capacitance combination represents a time constant whose dimensions agree with that of the basic element of the theory - relaxation time of the ionic atmosphere.

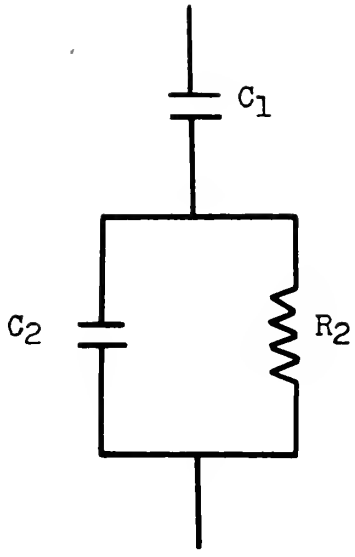
Now the physical makeup of the apparatus is examined. There is a cell which has a fixed capacitance and a fixed resistance and a solution with a variable capacitance and a variable resistance. Both these latter variables are functions of the low frequency conductance which in turn is related to the concentration. The resistance of the cell walls can be taken as being so high as to constitute an open circuit. The actual and equivalent circuits are shown in Fig. 3.

This approximate circuit gives rise to the equivalent circuit shown in Fig. 4.

It is now our problem to get expressions for C_p and R_p in terms of the measurable quantities C_w, C_s and R_s to compare theory with experimentally measured values of C_p and R_p. This resistance and capacitance is in reality the lumped sum of the individual ionic atmosphere characteristics giving an overall relaxation time to the solution. From the equivalent circuit it can be seen that the change in capacitance is to be handled by the C_p term as a function of low frequency conductance rather than on the basis of a change in the dielectric constant of the medium.



Actual Circuit



Approximate Circuit

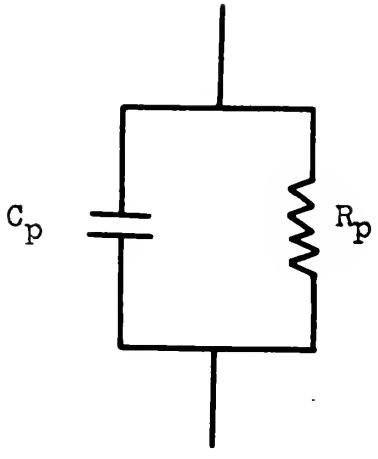
C_1 = Fixed capacitance of walls

C_2 = Capacitance of solution

R_2 = Resistance of solution = $\frac{1}{k}$

R_1 = Fixed resistance of walls

Figure 3



C_p = Equivalent parallel capacitance

R_p = Equivalent parallel resistance

Figure 4

Thus, the proposed circuit is a high loss (non-perfect) condenser with a charging and discharge time which is some function of the ionic relaxation time. Maximum power is transferred when energy is fed into the system in phase with its motion.

Since it is a function of the RC product which determines overall response, a measurement of this versus concentration would lead to a reasonable array of data. However, the problem of continuous measurement of such a product arises so it is broken up into its constituent parts of resistance and capacitance. The variation of each part with change in concentration is measured and the data interpreted in terms of the expressions for resistance and capacitance.

From the preceding development it can be seen that the concentration which gives a maximum power transfer corresponds to a certain time (i.e. relaxation time) which in turn corresponds to a certain RC product. In other words, in our circuit and in theoretical expressions, the maximum point on the power curve should correspond to a certain time which is a characteristic RC product. Since we have shown that power is directly proportional to the conductance for a given impressed voltage the maximum in the power curve versus concentration should correspond to the maximum of the high frequency conductance curve versus concentration.

Reilly and McCurdy (16) used elementary A-C analysis to arrive at workable expressions for the high frequency resistance

and capacitance. From the Debye-Falkenhagen equation and the identification of relaxation time with an RC product, the fact that high frequency conductance is a unique function of low frequency conductance is derived in the following manner:

1) $\frac{C_p}{G_p} = \frac{\text{Constant}}{\Lambda \times \gamma} = \Theta$

2) $\Lambda = \frac{1000 \times K_o}{\gamma}$ K_o = specific conductance

3) $\frac{C_p}{G_p} = \frac{\text{Constant}}{K_o}$

4) $G_p \propto K_o$

5) $k = K_o \frac{A}{l}$ where k = low freq. conductance
A = area of cellplates
l = distance between plates

6) $G_p \propto k$

Q.E.D.

The approximate circuit in Fig. 3 will now be analyzed.

1) Admittance of parallel elements:

$$Y_p = Y_r + Y_{c_2} = \frac{1}{R} + JWC_2$$

2) Admittance of series element = $Y_s = JWC_1$

3) $$Y_{total} = \frac{(\frac{1}{R} + JWC_2)(JWC_1)}{\frac{1}{R} + JWC_2 + JWC_1}$$

collecting terms

$$4)\quad Y_t = \frac{\frac{JWC_1}{R} - W^2C_1C_2}{1+JWRC_2 + JWRC_1}$$

rationalizing denominator

$$5)\quad \frac{\left(\frac{JWC_1}{R} - W^2C_1C_2\right)\left[\frac{1}{R} - JW\,(C_2+C_1)\right]}{\frac{1}{R^2} + W^2\,(C_2+C_1)^2}$$

multiplying numerator out the result is:

$$6)\quad \frac{JWC_1}{R^2} - \frac{W^2C_1C_2}{R} + \frac{W^2C_1(C_1+C_2)}{R} + JW^3(C_1+C_2)C_1C_2$$

collecting terms:

$$7)\quad \frac{W^2(C_1+C_2)C_1}{R} - \frac{W^2C_1C_2}{R} + J\left[\frac{WC_1}{R^2} + W^3C_1C_2\,(C_1+C_2)\right]$$

Placing numerator and denominator together:

$$8)\quad \frac{\frac{W^2C_1^2}{R} + J\left[\frac{WC_1}{R^2} + W^3C_1C_2^2+W^3C_2C_1^2\right]}{\frac{1}{R^2} + W^2\,(C_1 + C_2)^2}$$

Separating into real and imaginary parts and letting $\frac{1}{R} = k$ the result is:

$$9)\quad Y_t = \frac{kW^2C_1^2}{k^2+W^2(C_1+C_2)^2} + \frac{J\left[k^2WC_1+W^3C_1C_2^2+W^3C_2C_1^2\right]}{k^2+W^2(C_1+C_2)^2}$$

10) $Y_t = G_p + J\,B_p$ and $G_p = \frac{1}{R_p}$

$B_p = JWC_p$

11) $G_p = \frac{kW^2C_1^2}{k^2+W^2(C_1+C_2)^2}$ $\qquad C_p = \frac{k^2C_1+W^2C_1C_2\,(C_1+C_2)}{k^2+W^2(C_1+C_2)^2}$

This relationship leads to the equivalent circuit shown in Fig. 4.

At this point, some experimental data in the form of high frequency conductance curves will be introduced. The high frequency conductance is plotted as a function of K_o, the specific conductance for various impressed frequencies. As shown above: $K_o = \frac{\gamma\Lambda}{1000}$ so that the effect of changing the concentration can be noted by plotting K_o versus G_p. This gives rise to a universal curve depending only on the solvent but it is extremely important to note that in plotting the $\gamma\Lambda$ product the effect of the characteristic Λ of the electrolyte is masked. This masking effect will be noted later in the development of a characteristic constant for a given electrolyte.

It must be noted that, by a mathematical device, the qualitative determination potentialities of this phenomenon have been submerged.

The theoretical and experimental curves (16) are reproduced in figures 5 and 6.

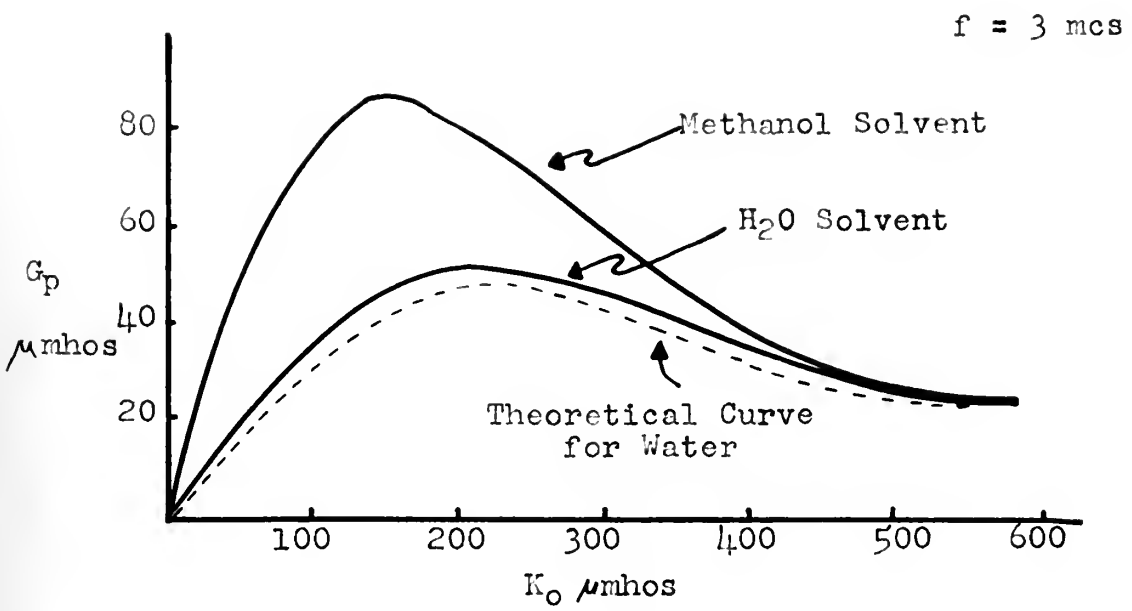


Figure 5

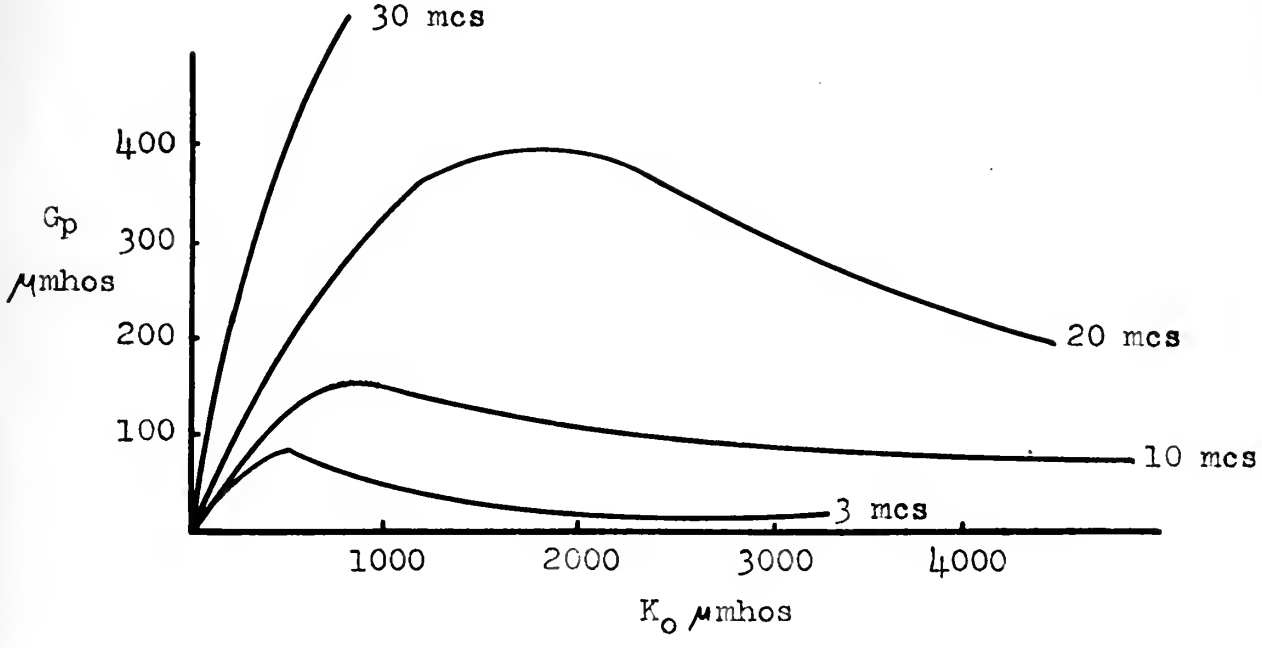


Figure 6

The theoretical curves were determined from the expression for G_p in equation (11) after measuring the static capacitances and assigning values to $K_o (= k \frac{l}{a})$. The error in G_p between theoretical and experimental values was attributed to lead capacitance and errors in measurement.

From equation (11) to find the value of G_p corresponding to its maximum value the following procedure is used:

$$\frac{dG_p}{dk} = \frac{(W^2C_1^2)(k^2+W^2(C_1+C_2)^2)-(kW^2C_1^2)2k}{k^2+W^2(C_1+C_2)^2} \qquad (12)$$

for k at which maximum G_p occurs:

$$\frac{dG_p}{dk} = 0; \quad W^4C_1^2(C_1+C_2)^2 = k^2W^2C_1^2 \qquad (13)$$

$$\text{or} \quad k = W(C_1+C_2) \qquad (14)$$

Then substituting for k in equation (11)

$$G_{p\ max} = \frac{WC_1^2}{2(C_1+C_2)} \qquad (15)$$

That equation (14) and the Debye-Falkenhagen equation are the same thing may be shown as follows:

$$k = W(C_1+C_2) \qquad (16)$$

$$C \frac{D}{} = \frac{D\ A}{3.6\times10^{12} \times \pi} \qquad (17)$$

$$k = K_o \frac{A}{l} \qquad (18)$$

Substituting:

$$K_o \frac{A}{I} = \frac{W\,(D_1+D_2)}{3.6\times10^{12}\pi}\left(\frac{A}{I}\right) \qquad (19)$$

Therefore

$$\frac{1}{W} = \frac{(D_1+D_2)}{K_o \times 3.6\times10^{12}\pi} \qquad (20)$$

Also

$$\frac{\Lambda\gamma}{1000} = K_o \qquad (21)$$

Substituting for K_o:

$$\frac{1}{W} = \frac{(D_1+D_2)\times1000}{\Lambda \times \gamma \times 3.6\times10^{12}\pi} \qquad (22)$$

Now at resonance, the condition imposed by equation (16) $\frac{1}{W} = \textcircled{H}$

$$\textcircled{H} = \frac{8.85\times10^{-11}\times(D_1+D_2)}{\Lambda \times \gamma} \qquad (23)$$

Equation (23) represents the relaxation time of the total system - cell plus solution. If we separate the solution by treating only D_2 we can obtain an expression for the relaxation time of the solution which may be compared with the Debye-Falkenhagen equation.

This approach yields:

$$\textcircled{H} = \frac{8.85\times10^{-11}D_2}{\Lambda \times \gamma} \qquad (24)$$

This is identical in form with the Debye-Falkenhagen equation although the dielectric constants and the equivalent conductances do not agree. We have, so far in this approach made no restrictions on the concentration of the electrolyte. If we now, as Debye and Falkenhagen did, assume very dilute solutions then:

$$D_2 \approx D_o \quad \text{(dielectric constant of solvent)} \qquad (25)$$

and $$\Lambda \approx \Lambda_\infty \qquad (26)$$

making these restrictions equation (24) becomes:

$$\textcircled{H} = \frac{8.85 \times 10^{-11} D_o}{\Lambda_\infty \times \gamma} \qquad (27)$$

Equation (27) is identical with the Debye-Falkenhagen equation and points out the restriction of dilute solutions in its applications.

Upon examining equation (16) it is seen that it can be put in the following form:

$$\frac{1}{W} = \frac{C_1+C_2}{k} \qquad (28)$$

Now $k = \frac{1}{R}$ and under condition of resonance imposed by equation (16) $\frac{1}{W} = \textcircled{H}$ equation (28) becomes:

$\textcircled{H} = R(C_1+C_2)$ (29) which upon neglecting the container becomes:

$\textcircled{H} = RC_2$ or a time constant associated with the D.C. characteristics of the solution.

Therefore, only at maximum power transfer does the relaxation time equal the D.C. time constant. The general expressions for R_p and C_p must have their product reduce to $\frac{1}{W}$ at the maximum power point in order for the time constant concept to have validity.

At this point Figures 5 and 6 will be briefly discussed in view of the foregoing theoretical considerations.

Discussion of k_{peak} equation

$$k = K_o \frac{A}{l} = W(C_2+C_1) \qquad (16)$$

a) Effect of solvent - If C_2 is increased by increasing the dielectric constant of the solvent then K_o peak will occur at a higher value. This corresponds to a higher concentration of electrolyte. This effect can be seen when the solvent is changed from methanol to water and the peak shifts to the right.

b) Effect of frequency - Increasing W moves K_o max further to the right.

Discussion of G_p peak equation

$$G_{p\ peak} = \frac{WC_1^2}{2(C_1+C_2)} \qquad (15)$$

a) Effect of solvent - If C_2 is increased by changing nature of solvent then the maximum value of G_p will be decreased as is shown in Fig. 5

b) Effect of frequency - Increasing frequency increases maximum value of G_p.

c) Cell constant (not shown) - Increasing $\frac{A}{l}$ will increase $G_{p_{max}}$ since:

$$G_{p_{max}} = \frac{W\, D_1^2 \left(\frac{A}{l}\right)^2 \text{ constant}}{2\, \frac{A}{l}\, (D_1+D_2) \text{ constant}}$$

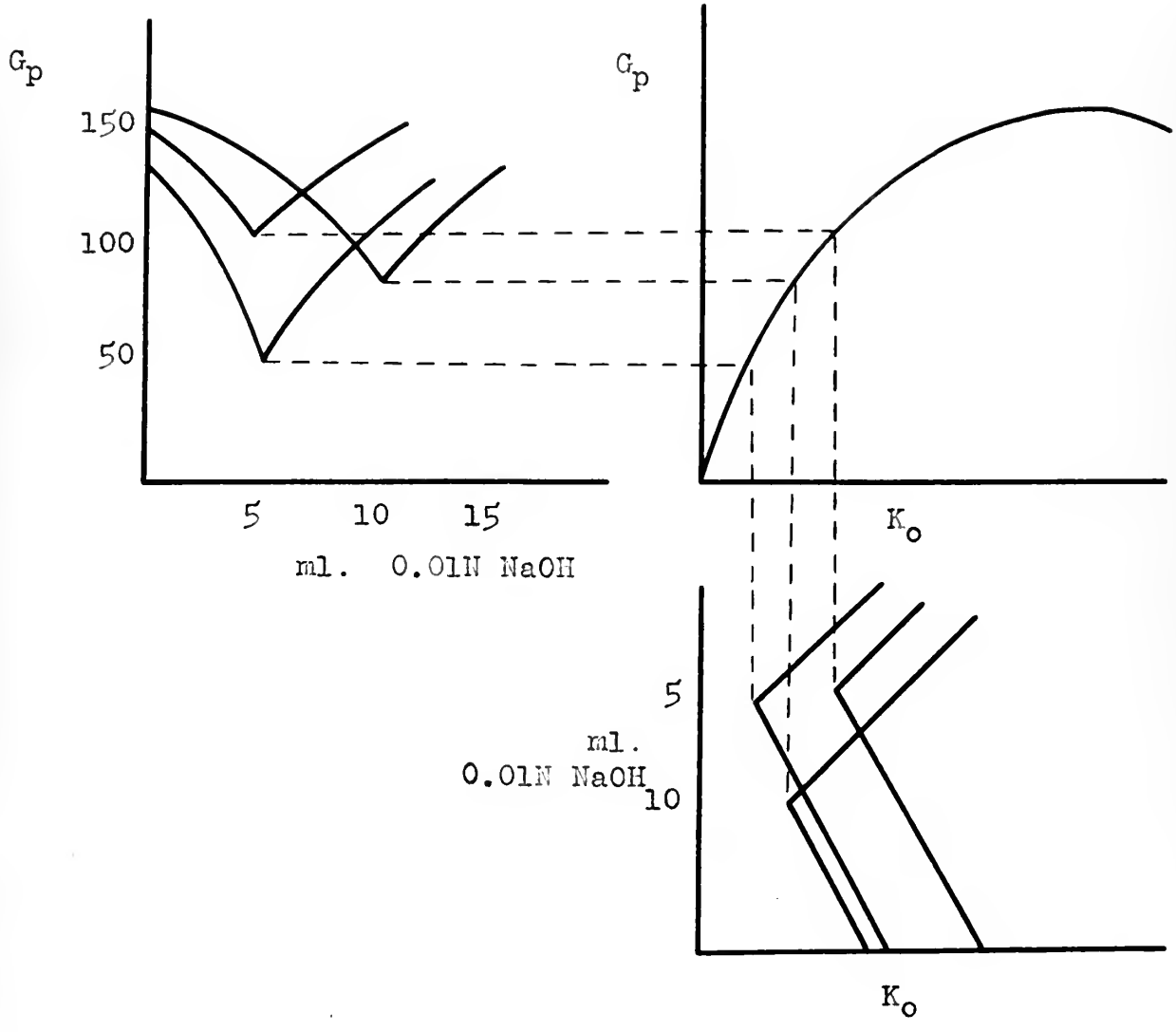
$$\text{or } G_{p_{max}} \propto \frac{A}{l}$$

Of interest in a titration, in addition to the above factors, is the range of maximum sensitivity i.e. when $\frac{dG_p}{dK_o}$ is a maximum. Mathematically this occurs when $\frac{d^2G_p}{dk^2} = 0$. Solving this equation for the value of k which gives maximum sensitivity the following expression is obtained.

$$k_{\text{max sensitivity}} = \sqrt{3}\, W(C_1+C_2) = \sqrt{3}\, k_{peak}$$

The same discussion under the k_{peak} equation applies here since the two are directly proportional.

Since it has been shown that the high frequency conductance is a unique function of the low frequency conductance, the high frequency titration curve can be related to the low frequency titration curves through this function. Reilly and McCurdy (16) have called the plot of such functions a transfer plot and used it as indicated in Figure 7.



Titration at 10 mcs.

Figure 7

This transfer plot is an orthographic projection of a three dimensional K_o, G_p and volume of reagent added surface as shown in Figure 8. These graphs are all drawn at a given impressed frequency.

The high frequency conductance having been investigated the high frequency capacitance will now be examined in the same manner to see if it varies according to the equivalent circuit parameters and the experimental curves. Upon examination of equation (11) it can be seen that the capacitance varies from a value of $\frac{C_1C_2}{C_1C_2}$ when $k \rightarrow 0$ to a value of C_1 when $k \rightarrow \infty$.

$\Delta C_{p_{max}}$ is found by subtracting the extreme values of C_p yielding:

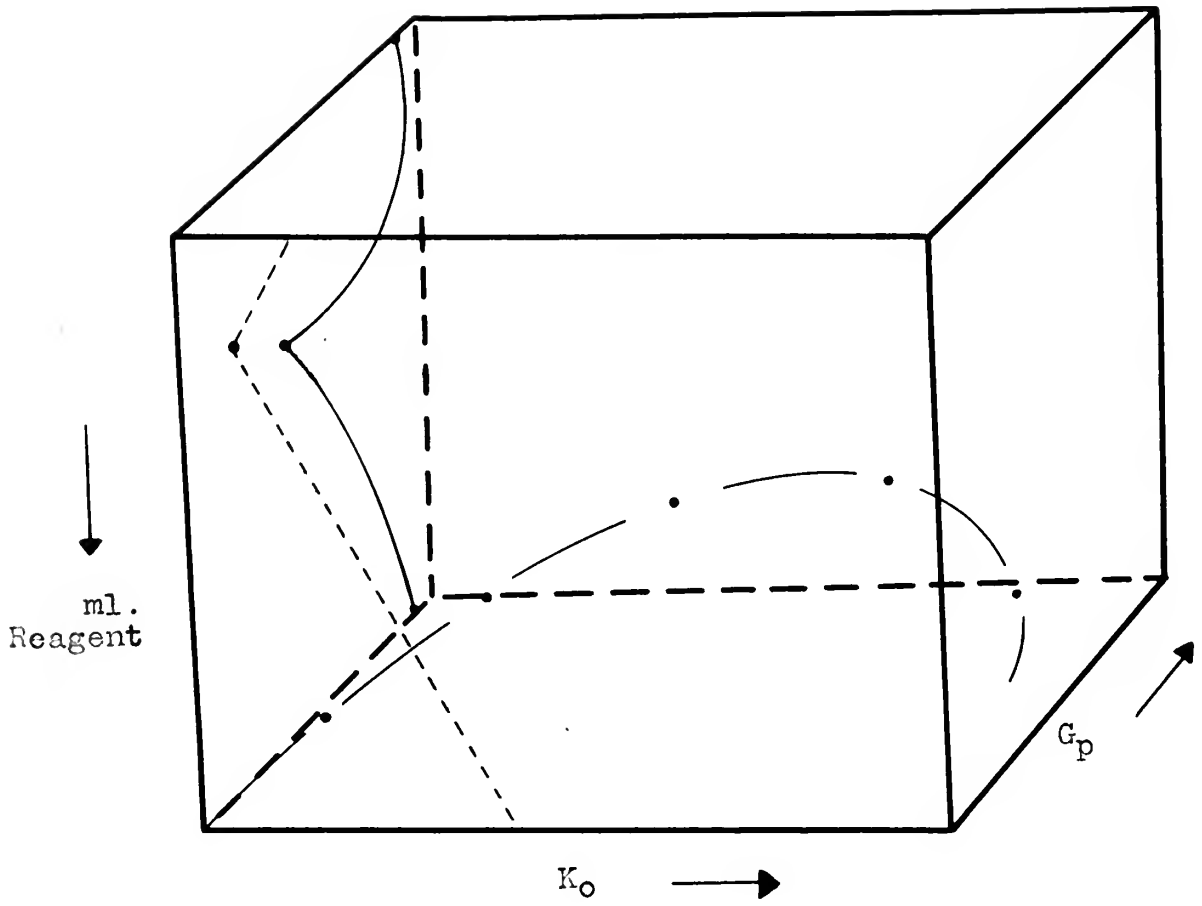
$$\Delta C_{p_{max}} = \frac{C_1 - C_1C_2}{C_1+C_2} = \frac{C_1^2}{C_1C_2} \qquad (29)$$

From examining equation (29) it can be seen that for a large value of ΔC_p, C_1 should be large and C_2 small.

The steepest slope is found as before from setting the second derivative of the expression for C_p from (16) equal to zero and solving. This yields:

$$k_{max\ sens.} = \frac{W(C_1+C_2)}{3} \qquad (30)$$

It can thus be seen that instruments responding to either conductance or capacitance changes have their maximum sensitivities occurring at different points.



—·—·—Reagent, K_o plane

---- G_p, K_o plane

—— G_p, reagent plane

Figure 8

To find the value of k corresponding to the midpoint of the C_p curves in order to check the Forman Crisp data the value of C at the midpoint is set equal to C_p and the resulting equation solved for k.

$$C_1 - \tfrac{1}{2}\Delta C_p = C_p \qquad (31)$$

This yields:

$$k_{M.P.} = W(C_1+C_2) \qquad (32)$$

which is in agreement with the previously stated prediction that the midpoint of the capacitance should be the point of resonance and correspond to the point of maximum conductance.

Transfer plots and curves similar in behavior to those of Figures 7 and 8 have been plotted and analyzed but will not be treated since the same general treatment as for conductance is applicable.

Instead, the validity of the premise that the relaxation time, Θ, is a time constant depending on the resonant values of the $R_p \Delta C_p$ product will be examined.

ΔC_p is used in lieu of C_p since the change in which we are interested is that due to the addition of solute - i.e. the value above the pure solvent value given by the expression for C_p when k approaches zero. In other words the pure solvent is taken as the zero point.

From equations (32) and (16) it has been shown that the values of G_p and ΔC_p corresponding to the restrictions of resonance occur at the same value of k. Further since $G_{p_{max}} = \frac{WC_1^2}{2(C_1+C_2)}$ (15),

and $\frac{\Delta C_p}{2} = \frac{WC_1^2}{2(C_1+C_2)}$ from equation (29) and that both these values correspond to resonance values, the R_p C_p product at this point should equal $\frac{1}{W}$ if the time constant concept is valid.

$$\left(\frac{\Delta C_p}{2}\right)\left(\frac{1}{G_p}\right) = \frac{C_1^2}{2(C_1+C_2)} \quad \frac{2(C_1+C_2)}{WC_1^2} = \frac{1}{W} = \textcircled{H} \qquad \text{Q.E.D.} \tag{33}$$

To add further weight to the premise that $\textcircled{H} = \Delta R_p C_p$ at conditions of resonance, the expression for power transfer in a high loss condenser is investigated. As before maximum power is the criterion of resonance.

$$P = (G_p + \tfrac{1}{2}\Delta C_p)\, E^2$$

Therefore the power is a maximum when the sum of G_p and $\frac{1}{2}\Delta C_p$ is a maximum which occurs at $G_{p_{max}}$ and $\frac{\Delta C_{p_{max}}}{2}$

Further, the power factor for the parallel circuit described is given by:

$$\text{Power factor} = \frac{1}{W \Delta R_p C_p} \tag{34}$$

The maximum power factor equals unity and should occur when maximum power is being dissipated, i.e. at the resonance conditions stipulated. From equation (33) it is seen that:

$$\Delta R_p C_p = \frac{1}{W} \quad \text{at resonance conditions}$$

Therefore, making this substitution in (34) the power factor under these conditions becomes:

$$\frac{1}{(W)\left(\frac{1}{W}\right)} = 1$$

This means physically that the relaxation time of the ionic atmosphere agrees with the period of the impressed alternating voltage. Further, it has been proved that the ionic relaxation time is the $\Delta R_p C_p$ product of the equivalent circuit operating at maximum power transfer conditions. This $\Delta R_p C_p$ product determines how well the ionic atmosphere follows the applied voltage since the natural frequency of the system is dependent on the DC parameters. If the relaxation time and the period of the impressed voltage coincide there is maximum power transfer - at any other point the ionic atmosphere cannot follow the field and losses occur.

This treatment attempts to tie the empirical curves of Forman and Crisp and the equivalent circuit proposed by Reilley and McCurdy together with the common bond of the relaxation time of the ionic atmosphere. This change of relaxation time is a function of the low frequency conductance and capacitance which are in turn functions of the concentration. Since C_p, the criterion of capacitance change, has as its only variable the low frequency conductance which varies with concentration, it can be seen that all variations in the circuit are expressed in terms of DC conductance. This also changes the dielectric constant of the medium since C_p can be expressed as:

$$C_p = \frac{D_p\, a}{1 \times 3.6 \times 10^{12} \pi}$$

It is again pointed out that K_o being a variable masks the characteristic value of the electrolyte which depends on the

equivalent conductance. Since it has been shown that:

$\lambda_{max}\ \gamma = K_e$ it can be seen that a measurement of the concentration and the frequency at which maximum absorption occurs could serve as a measure of the ionic species present. Some values of K_e have been tabulated (9) and do not seem to be sufficiently characteristic. However, refinements in technique might remove this difficulty in future determinations.

A further proof of the validity of the time constant concept is shown below utilizing data from Reilley and McCurdy (16).

1) At 3 MC $G_{p_{max}} = 50.0\ \mu$mhos

$C_{p_{max}} = 2.57$ mmf

2) If the peak $\Delta R_p C_p$ product equals $\textcircled{H}$ then the above product should equal $\frac{1}{W}$ within the error of the measurements.

3) $$\frac{1}{W} = \frac{\Delta C_p}{G_p} = \frac{2.57 \times 10^{-12}}{50 \times 10^{-6}}$$

4) Frequency = $$f = \frac{50 \times 10^{-6}}{2\pi \times 2.57 \times 10^{-12}} = 3.1 \text{ MC}$$

This value agrees with 3 MC within the claimed accuracy of the measurements (3.5%).

From the Debye-Falkenhagen equation it can be seen that for dilute solutions:

$$\textcircled{H} = \frac{C_{solvent}}{k}$$

To give exact correspondence between this equation and those developed from the equivalent circuit it must be noted that $C_{solvent}$

is not exactly the capacitance of the solution. It is true that the change is small (of order of 5 mmf), but the rate of change can be measured and is the basis for the ΔC_p versus K_o transfer plot. This change in the capacitance of the solution accounts for the "dispersion" of Forman and Crisp's experimental determination of the dielectric constant. By expressing the capacitance as C_p, a function of the concentration, it has been possible to allow for the variation of the capacitance while using fixed values for theoretical calculations. It has been shown previously how the dilute solution considerations can reduce the equivalent circuit equation to that of Debye and Falkenhagen.

The treatment of the theoretical circuit takes into account the change in dielectric constant with concentration since we measure in reality a "$\Delta \mathcal{D}$" from the solvent capacitance as the zero "ΔC_p" level. Therefore, the change in C_p is due to the departure from the dilute solutions which are postulated in the Debye-Falkenhagen theory.

By using K_o as a variable, the Λ versus Λ_∞ problem has been effectively sidestepped although the equations derived from the circuit show Λ and not Λ_∞ as the characteristic of the electrolyte.

From equation (11) the value of R_p is given below:

$$R_p = \frac{k^2+W^2(C_1+C_2)^2}{kW^2C_1^2} \qquad (11)$$

One general expression for ΔC_p is derived as follows:

$$\Delta C_p = C_p - \frac{C_1 C_2}{C_1+C_2}$$

$$\Delta C_p = \frac{k^2 C_1 (C_1+C_2) - C_1 C_2 k^2}{k^2 + W^2 (C_1+C_2)^2 \ (C_1+C_2)}$$

$$R_p \Delta C_p = \frac{k}{W^2 (C_1+C_2)} \qquad (35)$$

Equation (35) is the expression for the $R_p \Delta C_p$ product at any time and is therefore dependent on the frequency since both R_p and ΔC_p are dependent on frequency. At the resonant condition when $W = \frac{1}{\textcircled{H}}$ the $R_p \Delta C_p$ product becomes $\textcircled{H}$ as shown below:

$$R_p \Delta C_p = \frac{k}{W^2 (C_1+C_2)}$$

But at the resonant point from equation (16) $k = W(C_1+C_2)$.

Therefore, making this substitution in equation (35) the result is:

$$R_p \Delta C_p = \frac{W(C_1+C_2)}{W^2 (C_1+C_2)} = \frac{1}{W} \overset{D}{=} \textcircled{H} \text{ at resonance}$$

Therefore, it can be seen that although the general expression for the $R_p \Delta C_p$ product contains the frequency and the Debye-Falkenhagen equation does not; the two are related at the maximum power condition by $\textcircled{H} = \frac{1}{W}$. The relaxation time is independent

of the impressed frequency and depends only on the static parameters of the circuit.

In ordinary conductance measurements only the conductance variation with concentration is utilized while a high frequency conductance measurement points out the power relationship which varies for different impressed frequencies.

The change in low frequency capacitance with concentration is very small but the ΔC_p change is greater since frequency dependence is included in it. The contribution to the dielectric constant in dilute solutions is small with change in concentration but the contribution is not uniform but changes rapidly in the neighborhood of a resonant frequency analagous to the behavior of other circuit elements in this frequency range.

From an examination of Figure (8) it can be seen that the titrations can be made more accurate by proper selection of an impressed frequency. This suggests the use of variable frequency oscillators in this type of work.

The range of concentrations is dependent on the type of response of the instrument (G_p, ΔC_p) as can be seen from examining the equations. Therefore by using factors of cell design, solvent nature, and different type of measuring instrument all investigated at different frequencies an optimum combination can be reached for fast, accurate titrations and other determinations. (10)(6)(12)(2)

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